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Feature Article

Plant oils: The perfect renewable resource for polymer science?!

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ABSTRACT

Already for a long time, plant oils and their derivatives have been used by polymer chemists due to their renewable nature, world wide availability, relatively low price, and their rich application possibilities. Although many different synthetic approaches have been used, more recent examples are pointing in the direction of catalytic transformations and other efficient reactions to achieve a more sustainable production of polymers from these renewable resources. In this context, olefin metathesis, thiol–ene additions, and other processes can contribute not only to a more efficient synthesis of plant oil based polymers, but also to broaden the application possibilities of plant oils. This feature article provides an overview of the present situation with special attention to the use of olefin metathesis and thiol–ene chemistry as synthetic methods and as polymerization techniques.

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1. Introduction

Several arguments can be found to believe in the great potential of plant oils as an alternative resource for the production of polymeric materials [1]. The necessity of releasing the polymer industry from its dependence on depleting resources represents a major concern, pushing the search for industrially applicable renewable alternatives. In this context, plant oils offer many advantages apart from their renewability. Their world-wide availability and relatively low prices make them industrially attrac-

tive and feasible, as daily demonstrated with industrial oleochemistry. Furthermore, diverse chemistry can be applied on them, leading to a large variety of monomers and polymers [2]. Most importantly, the synthetic potential of nature is very high with this renewable feedstock and consequently, only a few minor modification reactions (if any at all) have to be performed in order to obtain suitable monomers for many different applications.

The main constituents of plant oils are triacylglycerols (triglycerides, see Fig. 1A), which are the product of esterification of glycerol with three fatty acids. Fatty acids account for 95% of the total weight of triglycerides and their content is characteristic for each plant oil (Fig. 1A). The structures of some frequently studied fatty acids are depicted in Fig. 1B.

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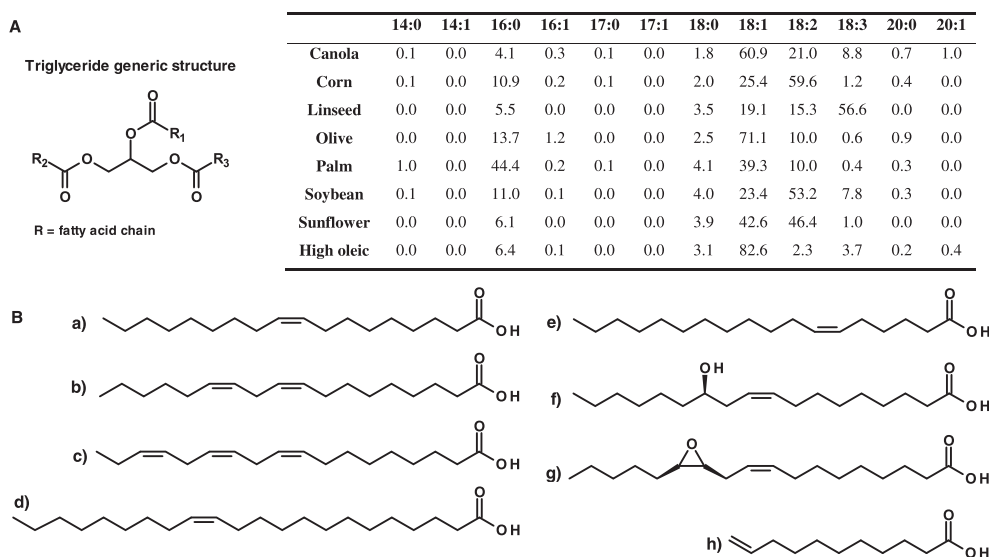


Fig. 1. (A) General triglyceride structure and fatty acid percentage composition of common plant oils (x:y stands for chain carbon atoms:number of unsaturations). (B) Fatty acids commonly used in polymer chemistry: (a) oleic acid, (b) linoleic acid, (c) linolenic acid, (d) erucic acid, (e) petroselinic acid, (f) ricinoleic acid, (g) vernolic acid, (h) 10-undecenoic acid.

Triglycerides are highly functionalized molecules, and, therefore, have been used in the synthesis of cross-linked polymers *via* two main approaches. The first one takes advantage of the naturally occurring functional groups present in triglycerides, such as internal double bonds, alcohols, or epoxides, which can be polymerized using different methods. The second strategy depends on chemical modifications prior to polymerization. This approach solves the drawback of the low reactivity of natural triglycerides (which usually only contain double bonds) by introducing easily polymerizable functional groups, and thus widens the synthetic possibilities. The hydrolysis of triglycerides provides glycerol and a mixture of fatty acids. Glycerol is a widely used building block in polymer science finding application in the synthesis of polyurethanes, polyesters, or telomers [3]. On the other hand, fatty acids have been used for a long time by polymer scientists for the development of polymeric structures, both directly and as building blocks for the synthesis of more sophisticated monomers [1].

2. Monomers and linear polymers from fatty acids

As mentioned above, either by simple hydrolysis or alcoholysis of triglycerides, fatty acids and esters can be easily obtained. Fatty acids are valuable renewable building blocks for the synthesis of designed monomers in the search for specific polymer properties that do not require extensive chemical modification prior to their application. Needless to mention that the latter argument is an important advantage not only in terms of sustainability, but also in terms of industrial feasibility. The wide chemistry that can be applied to fatty acids is reflected on the large amount of publications dealing with the use of fatty acids in the synthesis of valuable derivatives [4]. With regard to polymer science, recent contributions show a growing

interest in the use of fatty acids as precursors of monomers; not only because of their renewability, but also because of the properties they can provide to the final polymers. Therefore, we want to highlight some recent contributions to this field.

Concerning olefin metathesis, the double bonds present in fatty acids make them ideal starting materials for such transformations. Moreover, olefin metathesis cannot only be used for monomer synthesis, but also as polymerization technique. The ethenolysis of fatty acid methyl esters in the presence of Grubbs 1st generation catalyst was used by Warwel and coworkers for the preparation of ω -unsaturated fatty acid methyl esters. Taking these products as building blocks, they synthesized different polymers such as polyolefins, polyesters, and polyethers [5]. Moreover, Dixneuf and coworkers reported the efficient synthesis of methyl-9-decenoate, a useful precursor of ADMET monomers (see discussion below), through ethenolysis of methyl oleate in toluene and room temperature ionic liquids (RTILs) [6]. Different ruthenium alkylidene catalysts were used and catalyst recycling studies were performed with the first generation Hoveyda catalyst. Recently, Schrodi et al. evaluated the performance of several second generation NHC-based ruthenium olefin metathesis catalysts in the ethenolysis of methyl oleate [7]. They found better selectivity and activity for some of these catalysts than for the well known second generation Grubbs and Hoveyda–Grubbs catalysts, with TONs over 20,000.

Recently, Dixneuf et al. have reported the cross-metathesis (CM) of fatty acid derived unsaturated esters, acids, and aldehydes with acrylonitrile and fumaronitrile in the presence of Hoveyda–Grubbs 2nd generation catalyst [8]. These α,ω -bifunctional products can be transformed into valuable monomers like linear aminoesters, aminoacids, and aminoalcohols, through simple reductions. Another example from the same group showed the synthesis of

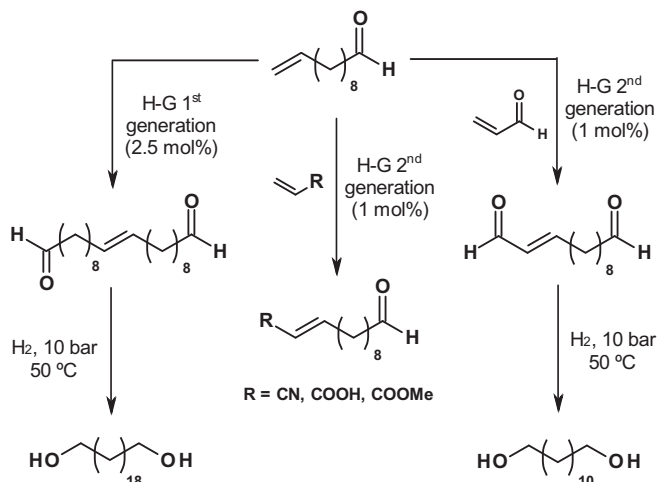


Fig. 2. Synthesis of saturated α,ω -diols and ω -functional aldehydes from 10-undecenal [9].

saturated C_{20} and C_{12} diols from castor oil derived 10-undecenal via either self-metathesis (SM) or CM with acrolein, acrylonitrile, acrylic acid, and methyl acrylate followed by hydrogenation in tandem catalytic reactions (Fig. 2) [9]. Also very recently, Dixneuf et al. have described the insertion of SnCl_2 into one Ru–Cl bond of Grubbs 1st generation and Hoveyda–Grubbs 2nd generation catalysts. The obtained Cl_3Sn –Ru-containing complexes presented very good alkene metathesis activities in the CM and SM of fatty acid derivatives [10].

Work in our group is also concerned with monomer synthesis applying metathesis chemistry to fatty acid derivatives. Fig. 3 depicts different building blocks prepared from fatty acid derivatives through self- and cross-metathesis, which are described in more detail later on.

In a first example, the bulk cross-metathesis of fatty acid methyl esters derived from plant oils with methyl acrylate was studied [11]. Grubbs and Hoveyda–Grubbs 2nd generation catalysts displayed very good activities with high conversions and CM selectivities. Nevertheless,

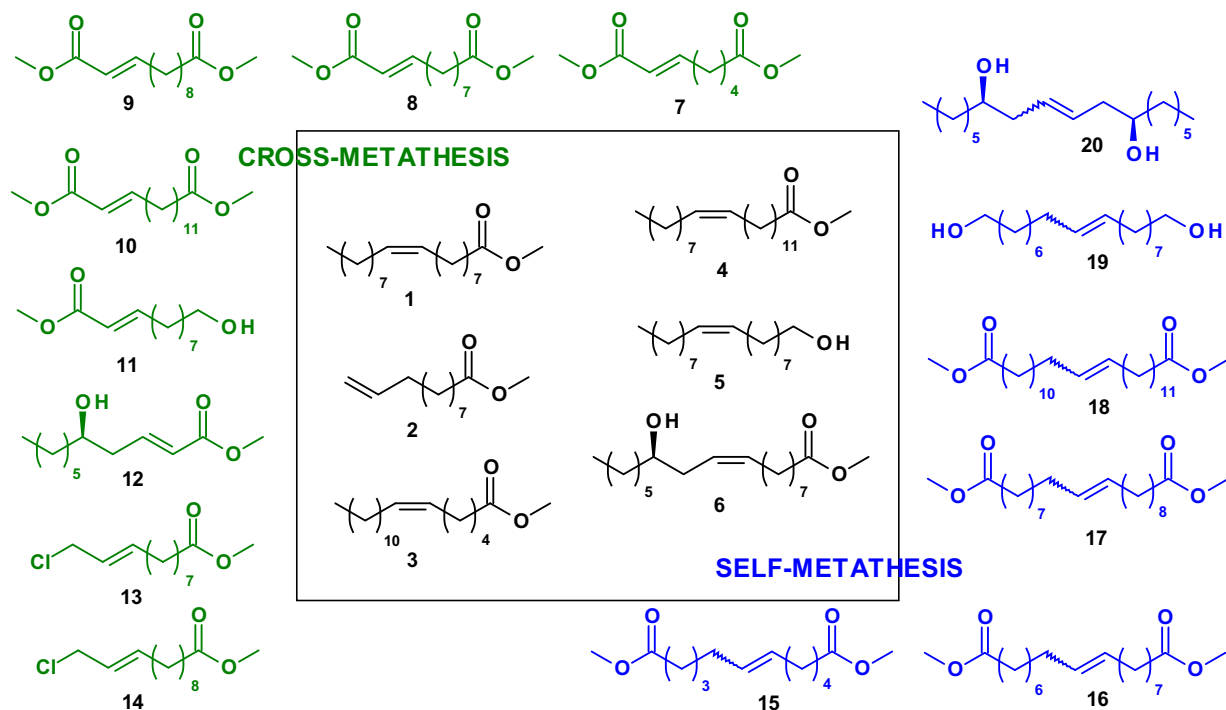


Fig. 3. Different monomers obtained from fatty acid derivatives by self-metathesis or cross-metathesis with methyl acrylate or allyl chloride [11,12,14,16,20].

the Hoveyda–Grubbs 2nd generation catalyst showed the best performance for both methyl oleate (**1**) (97% conversion, 92% CM product **8**, with 0.2 mol%) and methyl 10-undecenoate (**2**) (99% conversion, 99% CM product **9**, with 0.1 mol%). The same conditions were successfully applied to methyl erucate (**3**) and methyl petroselinatate (**4**). As a result, a family of unsaturated α,ω -diesters with chain lengths of 8, 11, 12, and 15 carbon atoms (CM products **7–10** in Fig. 3) and 12, 18, 20, 26 carbon atoms (SM products **15–18** in Fig. 3) were obtained. The former are interesting renewable monomers of potential industrial application for the synthesis of, e.g., polyesters or polyamides. On the other hand, the monofunctional cross-metathesis by-products are industrially relevant starting materials for detergent production. As an extension of these investigations, the production of α,ω -diesters *via* self-metathesis of **2** and its cross-metathesis with methyl acrylate was thoroughly studied [12]. Four different catalysts in loadings between 0.05 and 1 mol% were tested at temperatures ranging from 30 to 90 °C. Moreover, 1,4-benzoquinone was used to effectively suppress olefin isomerization side-reactions [13]. Double bond isomerization occurring during the diesters syntheses leads to irregular chain lengths and was mainly observed when second generation catalysts and high temperatures were used. The best conditions found for the synthesis of the 20-carbon diester **17** were 0.05 mol% of Hoveyda–Grubbs 2nd generation catalyst, 0.1 mol% of benzoquinone, and continuous vacuum at 50 °C. Under such conditions, the conversion reached 84.5% with only 3.1% isomerization. As explained above, the cross-metathesis of **2** and methyl acrylate can be easily performed reaching full conversions and high CM selectivity if 5- to 10-fold excess of methyl acrylate is used. However, in order to meet green chemistry requirements, the synthesis of **11** was also optimized for a 1:1 ratio between both reactants. Interestingly, also with this restriction highly efficient reaction conditions could be found; conversions over 97% and CM selectivities over 90% were obtained with both Hoveyda–Grubbs 2nd generation and Zhan catalysts.

In related work, the bulk cross-metathesis reaction between oleyl alcohol (**5**) and methyl acrylate was performed and optimized to combine high conversion and cross-metathesis selectivity [14]. The Hoveyda–Grubbs 2nd generation catalyst was the best suited for these reactions and was thus used throughout the whole study. The results revealed that 5 mol% catalyst load and a 5-fold excess of methyl acrylate was necessary to reach a conversion and cross-metathesis selectivity over 90%. To overcome the problem of catalyst poisoning, the hydroxyl group was protected as acetate. The catalyst demand was thus reduced obtaining quantitative conversions and 96% cross-metathesis selectivity with 1 mol% catalyst when a 5-fold excess of methyl acrylate was used. Moreover, using a 10-fold excess of methyl acrylate provided similar results with 0.5 mol% catalyst. The obtained difunctional derivatives (**11** and **19**, Fig. 3) are suitable monomers for polyester synthesis. Furthermore, both approaches were compared regarding their environmental impact using EATOS (environmental assessment tool for organic syntheses) [15]. The mass index S^{-1} (mass of all raw materials used for

the synthesis per mass unit of the purified product) and the environmental factor E (waste per mass unit of the product) were thus obtained for the different reactions performed. These factors would be minimal in an ideal case of maximum sustainability. For these reactions, the results revealed that the protecting group strategy is necessary to reduce the overall waste generation, and that the recycling of unreacted starting materials significantly reduces the environmental impact. The protection of the hydroxyl group, however, was not necessary in the cross-metathesis of methyl ricinoleate with methyl acrylate, most likely due to the lower reactivity of the secondary alcohol towards the catalyst. In contrast to methyl oleate, the CM of methyl ricinoleate (**6**) results in two difunctional compounds (**12** and **20**, Fig. 3) [16]. The reaction conditions were optimized for Hoveyda–Grubbs 2nd generation and Zhan catalysts using a design-of-experiment (DoE) approach which, requiring only a small number of experiments, provided information about the most important reaction parameters, thus allowing their optimization. The DoE approach also allowed to easily establish the different response of each catalyst towards the reaction parameters.

In a remarkable contribution by Cole–Hamilton and coworkers, an alternative method to obtain an α,ω -diester from methyl oleate was described [17]. The process involved the methoxycarbonylation of unsaturated acids or esters using a palladium based catalyst and a designed ligand, *bis*(di-*tert*-butylphosphinomethyl)benzene, to selectively produce α,ω -diesters independently of the initial position of the double bond [17]. This reaction was recently optimized and applied by Quinzler and Mecking for the synthesis of dimethyl 1,19-nonadecanedioate from methyl oleate [18]. This α,ω -diester was polymerized by reaction with its diol reduction product in the presence of titanium alkoxides. The polyester thus obtained showed a molecular weight of around 20 kDa. In another example, Jackson and coworkers showed the conversion of natural oils into α,ω -dicarbonylic compounds by a one pot reaction sequence of CM with 2-butene followed by isomerization, methoxycarbonylation, and transesterification [19].

Another approach to α,ω -difunctional monomers consisted in the cross-metathesis of allyl chloride with methyl oleate and methyl 10-undecenoate [20]. The objective of this work was to show the synthesis of plant oil based building blocks potentially useful for Nylon-11 and Nylon-12 production (**13** and **14**, Fig. 3), and to demonstrate the possibility of performing these transformations with high efficiency. From a screening of several reaction conditions using Hoveyda–Grubbs 2nd generation and Zhan catalysts, it was observed that both catalysts performed similarly well at low catalyst loadings (70–80% CM selectivity with 0.5–1 mol%). This procedure represented an improvement over previous reports on cross-metathesis of allyl halides due to the solvent-free conditions used, which permitted to lower the catalyst loading and gave higher reaction rates.

Olefin metathesis has also been exploited as the polymerization method for the production of renewable polymers from fatty acid derived monomers. Acyclic diene metathesis (ADMET) is a step-growth polymerization, usually performed on α,ω -dienes, which is driven by the

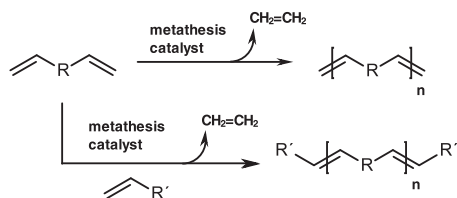


Fig. 4. General scheme of ADMET polymerization, and ADMET polymerization in the presence of a generic chain-stopper in the synthesis of end-group functionalized polymers.

release of ethylene as condensate (Fig. 4) [21]. The polymers produced *via* ADMET are strictly linear with unsaturated backbones and, depending on the reaction conditions, possess well-defined structures.

Key to the purpose of applying ADMET to fatty acid derivatives has been the use of 10-undecenoic acid as the building block for monomer synthesis. This very interesting compound can be obtained from castor oil *via* pyrolysis [22] and is the industrial intermediate for the synthesis of Nylon-11. It contains a terminal double bond that makes it suitable for the design of α,ω -diene monomers. Moreover, different commercially useful building blocks are derived from 10-undecenoic acid, such as methyl-10-undecenoate, 10-undecenol, or 10-undecenoyl chloride. Fig. 5 shows different fatty acid based monomers that have been synthesized and used to produce polymers *via* ADMET. The following paragraphs discuss the most important aspects of these investigations.

In one of our examples, by simple esterification of 10-undecenoic acid with 10-undecenol, a new α,ω -diene monomer (**21**, Fig. 5) was obtained and subsequently polymerized *via* ADMET in the presence of Grubbs and Hoveyda–Grubbs 2nd generation catalysts [23]. The Grubbs 2nd generation catalyst displayed the best results affording polyesters of 22,000 and 26,500 Da with 0.5 and 1 mol% of

catalyst, respectively. Moreover, methyl-10-undecenoate was added to the initial reaction mixture as chain-stopper, thus providing a simple method to control the molecular weight of the polyesters. The integration of the resulting methyl ester end-groups in the ^1H NMR spectra further allowed calculating the absolute molecular weights. Furthermore, by changing the nature of the chain stopper, designed end-group functionalized polymers should be easily obtained. To prove this, an oligomeric poly(ethylene glycol) methyl ether acrylate was successfully used as monofunctional chain-stopper in the one-step one-pot synthesis of an ABA triblock copolymer.

One of the main concerns about the use of polymeric materials is their flammability, which annually causes huge human and material losses [24]. For this reason, fire retardants such as phosphorus or silicon are usually introduced into polymers to reduce the risk of fire initiation and/or spreading [25]. The possibility of inferring flame retardancy to the renewable polyesters described above was explored by introducing a phosphorus-containing comonomer, also having two 10-undecenoic moieties linked to a heteroaromatic core (**22**, Fig. 5) [26]. Linear random copolymers were thus synthesized using 1 mol% of Grubbs 2nd generation catalyst. The ratio of both monomers was systematically varied to gain insight into the phosphorus content/flame retardance relationship and the effect of phosphorus on the performance of the catalyst. Several conclusions could be drawn from this study. First, the catalyst was not appreciably affected from the presence of the phosphorus moiety, and molecular weights up to 38 kDa were obtained. Second, the polymerization temperature dictated the homogeneity of the molecular weight distributions and the catalyst activity, and third, an increase in the phosphorus content from 0.00 to only 3.12 wt% resulted in an increase of the limiting oxygen index (LOI) [25] value from 19.0 to 23.5.

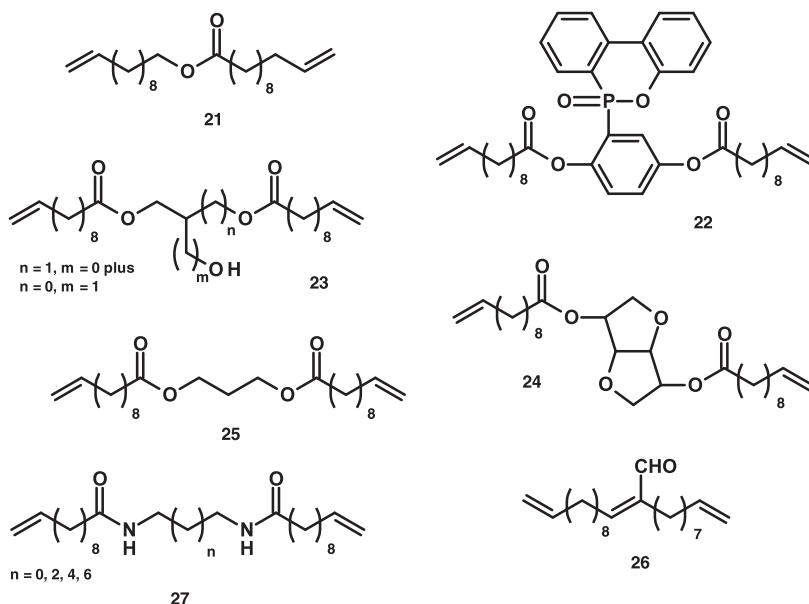


Fig. 5. Different fatty acid based monomers used for ADMET polymerizations [23,26,27,29–33].

ADMET polymerization has been extensively used for the production of linear polymers, however, relatively little work has been directed to the synthesis of cross-linkable polymers for the production of thermosetting materials [21]. ADMET offers a convenient way to obtain macromolecules bearing polymerizable groups along the backbone through monomer design. Thus, the only requirement is to find a metathesis catalyst being compatible with the functional group introduced to the α,ω -diene structure. This approach has been used in the synthesis of plant oil based flame retardant thermosets [27]. An α,ω -diene containing a pendant hydroxyl group (**23**, Fig. 5) was synthesized using 1,3-dichloropropan-2-ol, which can be glycerol derived [28], and 10-undecenoic acid. In order to provide flame retardancy, **22** was used as comonomer. Grubbs 2nd generation catalyst was used in the homopolymerization and Hoveyda–Grubbs 2nd generation catalyst was used in the random copolymerizations leading to molecular weights over 18,000 g/mol (calculated from ^1H NMR integrations). The amount of phosphorus in the linear copolymers was modified by varying the monomer feed ratio, and in the second step the remaining hydroxyls of the obtained copolymer series were acrylated to introduce cross-linkable sites along the backbone. The radical polymerization of these polymers afforded highly cross-linked thermosets with glass transition temperatures ranging from 35 to 52 °C. These materials were shown to be stable up to 340 °C and gave, in good correlation with the phosphorus content, char yields (at 800 °C) up to 11.2%, and an increase of the LOI value from 18.4 to 25.7 despite their high fatty acid content. Moreover, tensile tests revealed pronounced differences in the mechanical properties due to the differences in the cross-link densities and compositions, revealing, for example, elongations of 5% and 142% for the homopolymer and the copolymer with maximum phosphorus content, respectively.

One of our investigations took advantage of the degradability of a fatty acid/carbohydrate based polyester to gain knowledge about double bond isomerization side reactions taking place during ADMET polymerization [29]. Different metathesis catalysts and reaction conditions affecting double bond isomerization were applied for the ADMET polymerization of a 10-undecenoic acid based α,ω -diene (**24**, Fig. 5). The 100% renewable polyesters thus obtained were subsequently transesterified with methanol, and the resulting products, representing the repeating units of each polymer, were analyzed by GC–MS (Fig. 6). In this way, the quantitative determination of the amount of isomerization side reactions was possible. The results showed that Grubbs 1st generation catalyst promoted little olefin isomerization up to 90 °C (<5%). However, the isomerization behaviour of Grubbs 2nd generation catalyst clearly depended on the reaction temperature resulting in isomerization degrees up to 76%. This method provided an easy way to quantify isomerization side reactions during ADMET polymerization, which up to that moment was a difficult task due to the limitations of polymer analysis techniques.

As shown by Grubbs and coworkers, olefin isomerization during metathesis reactions can be prevented with 1,4-benzoquinone [13]. The effect of this additive on the

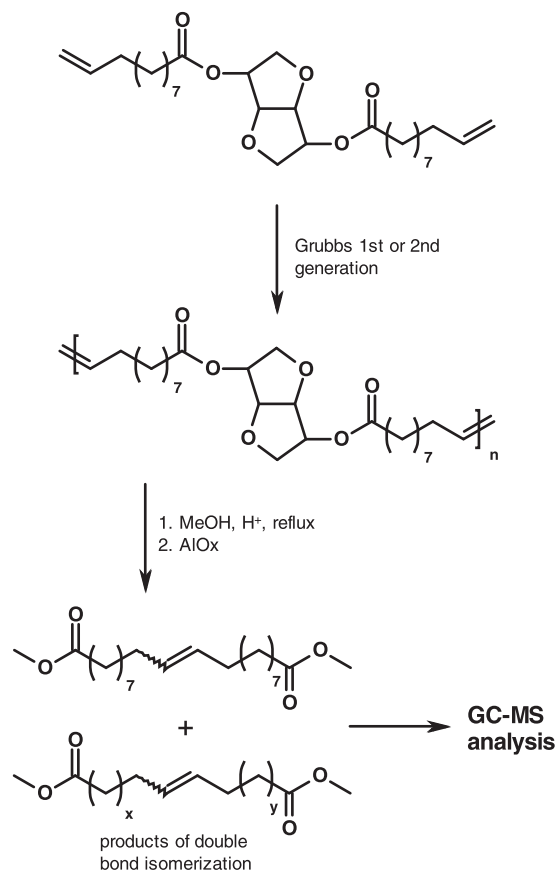


Fig. 6. Procedure for the quantification of double bond isomerization during ADMET. Polymerization, degradation, and GC–MS analysis of transesterification products [29].

isomerization behaviour of second generation metathesis catalysts during ADMET was thus investigated [30]. For this study, a 100% renewable monomer (**25**, Fig. 5) was synthesized from 10-undecenoic acid and 1,3-propanediol, which can be obtained by fermentation of glycerol. The isomerization degree was determined following the aforementioned procedure of polymer transesterification followed by GC–MS analysis. It was shown that the use of only 2 mol% of 1,4-benzoquinone can reduce olefin isomerization from 90% to below 7%. Most recently, also indylidene based catalysts were evaluated for their isomerization tendency using the same monomer and method [31]. These catalysts showed significantly higher isomerization degrees than their benzyldiene counterparts. Moreover, it could be shown that benzoquinone is not efficient in suppressing the isomerisation for these catalysts.

Another interesting building block obtained by reduction of 10-undecenoic acid is 10-undecenal. The self-aldol condensation of 10-undecenal under basic conditions was recently performed to obtain an α,ω -diene containing an α,β -unsaturated aldehyde (**26**, Fig. 5) [32]. The ADMET polymerization of this monomer was investigated at 80 °C in the presence of several metathesis catalysts. Moreover, 3 mol% of 1,4-benzoquinone (related to catalyst) was added to reduce the isomerization side-reactions. Four out

of nine metathesis catalysts tested showed good metathesis activity despite the aldehyde group. Furthermore, it was also possible to reduce the aldehyde groups after polymerization to obtain a poly(allyl alcohol), which could allow for further functionalization or cross-linking.

The synthesis of polyamides was also attempted via ADMET polymerization of a series of α,ω -dienes containing two secondary amides (**27**, Fig. 5) [33]. These monomers were synthesized via catalytic amidation of methyl 10-undecenoate with aliphatic diamines of varying chain length. However, the ADMET polymerization of these monomers was unsuccessful. The high melting point and polarity of the monomers made it necessary to perform the polymerizations in strongly coordinating high boiling point solvents like DMF or DMSO, which are not well tolerated by metathesis catalysts. Under these conditions, even catalyst loadings as high as 10% only yielded oligomers. For this reasons, the strategy was reversed. Thus, the self-metathesis of methyl-10-undecenoate (see discussion above) was first performed to obtain a diester that was then polymerized with diamines using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. This new strategy afforded renewable polyamides **X**,20 with molecular weights (M_n) up to 14,700 Da in the presence of 5 mol% of TBD. This polyamide synthesis presents advantages over traditional techniques such as the avoidance of acid chlorides.

Also in the field of olefin metathesis, ring opening metathesis polymerization (ROMP), which features the characteristics of a living polymerization, is a powerful tool for the direct synthesis of well defined polymers [34]. Norbornene and its functionalized derivatives are typically used in ROMP due to commercial availability, low cost, and general ease of synthesis. Norbornene monomers functionalized with a series of fatty acids of chain lengths from C_6 to C_{18} , were synthesized and polymerized via ROMP in the presence of Grubbs 3rd generation catalyst (Fig. 7) [35]. The polymerizations showed living behaviour leading to polymers with molecular weights up to 126 kDa and polydispersities between 1.05 and 1.26 depending on the reaction conditions. The length of the fatty acid chain strongly determined the thermal properties of the polymers. Thus, as the chain length was varied from 6 to 18

carbons, the T_g decreased from 102 to -32 °C. Moreover, only the polymers bearing chains between 14 and 18 carbon atoms were able to crystallize, showing a decrease in the T_m with the chain length increase (from 30 to 6 °C). Regarding the thermal stability, all polymers were stable below 325 °C due to their similar structure.

We were also able to prepare well defined main chain substituted polymethacrylates by copper-mediated atom transfer radical polymerization (ATRP) of fatty alcohol derived methacrylates [36]. The reaction conditions were optimized for the bulk polymerization of lauryl methacrylate, being thus possible to obtain poly(lauryl methacrylate)s with targeted degrees of polymerization in a controlled fashion. With the optimized system, conversions over 90% and narrow polydispersities were obtained working at 35 °C. This system was also successfully applied to the controlled polymerization of methacrylates functionalized with fatty acid chains of different lengths (C_{10} to C_{18}). The polymers containing fatty acid chains between 12 and 16 carbons were able to crystallize, showing an increase of the T_m values from -40 to 19 °C with the increase of the alkyl chain lengths. A further increase of the chain length to 18 carbons yielded a polymer with a T_m of 47 °C, which, due to the polymerization temperature (35 °C), precipitated from the reaction mixture leading to a less defined polymer. All studied polymers presented similar thermal stability with main degradation steps starting *ca.* 330 °C.

The thiol–ene addition is a well established reaction that is known for more than 100 years. Currently, it is undergoing an intense revival in many areas of chemistry [37]. With respect to polymer chemistry, this transformation has been used as polymerization technique and for efficient post-polymerization modifications [37,38]. Several examples of thiol–ene reactions with plant oils and fatty acids have been reported, but interestingly, only a few deal with the synthesis of fatty acid derived monomers and/or to their polymerization. First Koenig and Swern [39], and later on Metzger and Riedner [40], published the synthesis of α,ω -dicarbonylic oleic acid derivatives through thiol–ene additions using thiols and dithiols. More recently, taking methyl oleate and methyl linoleate as substrates, Samuelsson et al. [41] studied the effect of

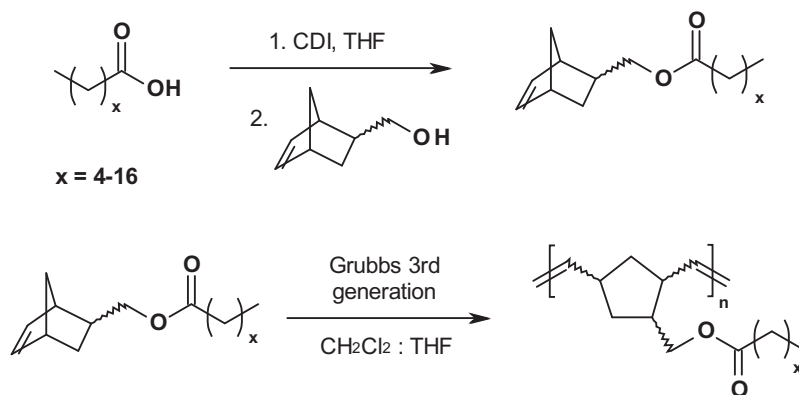


Fig. 7. Synthesis of fatty acid substituted norbornenes and their ROMP [35].

weights ranging from 1000 to 3000 g/mol, and with hydroxyl, carboxyl, or trimethoxysilyl end-groups were synthesized. Moreover, a hydroxyl terminated telechelic ($M_n^{\text{NMR}} = 3100$ g/mol) could be applied as a soft segment in the synthesis of a thermoplastic segmented poly(ester urethane).

Our group has also contributed to this field with the preparation of a set of 10-undecenoic acid derived monomers *via* thiol–ene additions (Fig. 9) [43]. These reactions were carried out in absence of solvent and initiator, and gave good to excellent yields. The α,ω -difunctional monomers prepared, containing methyl ester and/or hydroxyl groups, were polymerized using TBD as catalyst to obtain a family of linear and hyperbranched polyesters with molecular weights (M_n) between 4000 and 9500 Da. When methyl 10-undecenoate was reacted with thioglycerol, an AB_2 monomer was obtained and used for the synthesis of hyperbranched polyesters in the presence and in absence of glycerol as core molecule. Regarding the thermal stability and properties of these polyesters, all of them were stable up to 300 °C and showed T_m values ranging from 50 to 70 °C.

Fatty acids have also found application in polyoxazoline synthesis. A soybean oil based 2-oxazoline (SoyOx) monomer has been used by Hoogenboom and Schubert in the preparation of well defined polymers *via* microwave-assisted cationic ring-opening polymerization (ROP) [44]. The possibility of the double bonds of the fatty acid side chains to undergo UV cross-linking was also explored. For this purpose, a series of statistical copolymers (PDI <1.38) of SoyOx and 2-ethyl-2-oxazoline (EtOX) were subjected to UV-curing, observing that 5 mol% of SoyOX was enough to provide efficient cross-linking [45]. Furthermore, amphiphilic block copolymers of SoyOX and EtOX were used to prepare aqueous spherical micelles, which were further cross-linked by UV irradiation. These cross-linked micelles showed a change in their morphology, from spheres to short rods, when transferred from water into acetone [46]. Very recently, the ROP of epoxidized methyl oleate with ionic-coordinative initiators has been thoroughly studied by del Rio et al. By means of MALDI-TOF-MS, SEC, and ^1H and ^{13}C NMR, they could establish that the products obtained consisted in a complex mixture of cyclic and linear polymeric structures [47]. Depending on the catalyst used different chain ends were found, a fact that was related to the occurrence of two competitive propagation mechanisms, namely, cationic and ionic-coordinative. The polymers obtained, having higher molecular weights (up to 7000 Da) than those obtained with conventional cationic catalysts, were used for the synthesis of poly(ether urethane)s by reaction with 4,4'-methylenebis(phenyl isocyanate) or L-lysine diisocyanate [48]. Furthermore, segmented poly(ether urethane)s with various hard segments were prepared by addition of 1,3-propanediol as chain extender. As a result, a wide family of cross-linked materials was obtained with glass transition temperatures ranging from –30 to 60 °C, good thermal stability below 300 °C, and tensile modules between 1 and 74 MPa.

Using a different approach, Lligadas et al. reported the synthesis of aromatic triols *via* palladium-catalyzed trimerization of internal or terminal alkyne fatty acid methyl

esters, and subsequent reduction of the ester groups [49]. Since non-symmetric alkynes were used, the trimerization led to a mixture of the symmetric and unsymmetric trimers. These biobased triols were used in the preparation of polyurethane networks. Using the same palladium-catalyzed trimerization, Narine and coworkers prepared triols from oleic and erucic acids, being able to separate the symmetric and unsymmetric products by flash chromatography [50]. Work in Narine's group has been recently directed to the synthesis of diisocyanates from methyl oleate either *via* ozonolysis [51] or self-metathesis [52] followed by Curtius rearrangement. Reaction of this diisocyanates with mixtures of canola oil derived polyols provided different biobased polyurethanes. Furthermore, following a similar procedure they recently prepared fully fatty acid based diols from methyl oleate, which were reacted with 1,7-heptamethylene diisocyanate, also from methyl oleate, to produce thermoplastic polyurethanes entirely from fatty acid resources [53].

Narine et al. have also reported the preparation and ROP of lactone monomers from 9-hydroxynonanoic acid, which was synthesized from methyl oleate *via* an ozonolysis/hydrogenation/saponification based methodology (Fig. 10) [54]. The biodegradability and drug delivery properties of

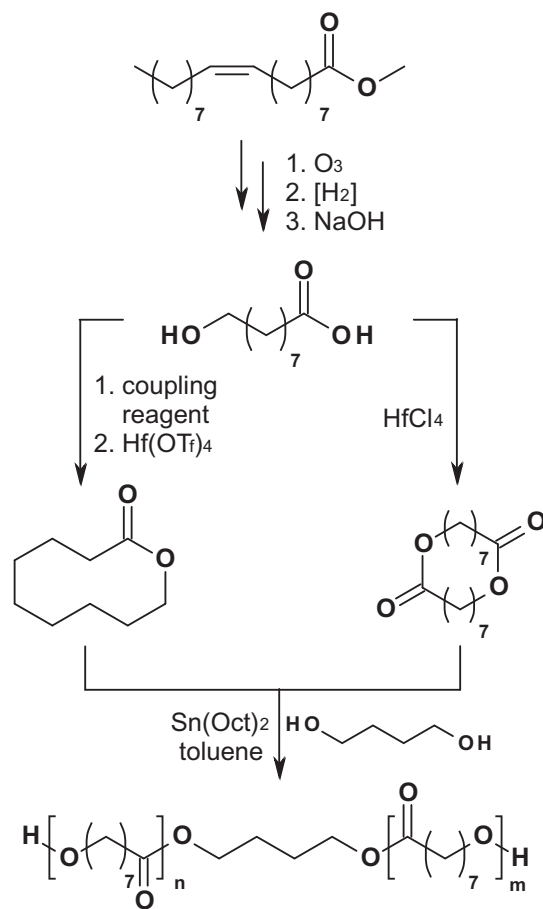


Fig. 10. Synthesis of lactone and dilactone structures from methyl oleate and their ROP [54,55].

the poly(nonanolactones) thus obtained were evaluated, confirming them as good candidates to replace petroleum based polycaprolactone [55]. The introduction of plant oil derivatives in biodegradable polymers provides flexibility, lowers the melting temperature, and increases hydrophobicity and pliability [56]. Moreover, these polymers produce benign degradation products, which make them suitable for various medical applications like drug delivery and temporary implantable devices. Domb and coworkers have shown that inclusion of fatty acids in polymers retard the degradation and release of incorporated drugs. Moreover, they prepared a bifunctional ricinoleic acid derivative which, upon incorporation into either polyanhydride or copolyester, provided a wide range of biomaterials from solid implants to *in situ* forming injectable gels [56].

3. Hyperbranched and cross-linked polymers from plant oils

The direct use of plant oils for the synthesis of hyperbranched (hb) polymers has a short course, entirely centered on acyclic diene metathesis (ADMET) polymerization. However, the high functionality of triglycerides together with the fact that all double bonds present similar reactivity make this polymerization very difficult to control, usually yielding cross-linked structures. Acyclic diene metathesis (ADMET) polymerization of plant oils was traditionally performed in the presence of the catalytic system $WCl_6-(CH_3)_4Sn$, which presents poor stability towards moisture and oxygen. Moreover, solvent and high

catalyst loads were needed [57]. Later on, Larock and coworkers overcame this problem switching to the much more efficient Grubbs 1st generation metathesis catalyst (C1) [58]. The high metathesis activity of this complex enabled the ADMET polymerization of different plant oils to alcohol-insoluble oligomers with catalyst loadings as low as 0.1 mol%. Subsequently, a thorough study of the products obtained in the ADMET polymerization of plant oils was performed using glyceryl trioleate as model compound [59]. Trimer, tetramer, pentamer as well as monocyclic oligomers were identified using metathesis catalyst C1. A further step towards control in the ADMET of plant oils was recently reported with the use of methyl acrylate as chain stopper. By performing the ADMET of a model triglyceride in the presence of different amounts of methyl acrylate, cross-linking was avoided and thus, hb polymers could be obtained in a one step procedure [60]. Since the triglyceride used was trifunctional, this procedure was defined as acyclic triene metathesis (ATMET) polymerization. Furthermore, this strategy permitted to tune the size of the polymers by the amount of chain stopper used, and more interestingly, this method could allow the direct synthesis of end-group functionalized hb polymers by simple choice of the chain stopper. Once proved with a model compound, ATMET polymerization was applied to high oleic sunflower oil as a direct way to hb polymers from naturally occurring plant oils (Fig. 11) [61]. In opposition to the model reaction in which ethylene was released, constant vacuum was applied throughout the ATMET of high oleic sunflower oil to facilitate removal of 9-octadecene and shift the reaction equilibrium to product formation. The products obtained

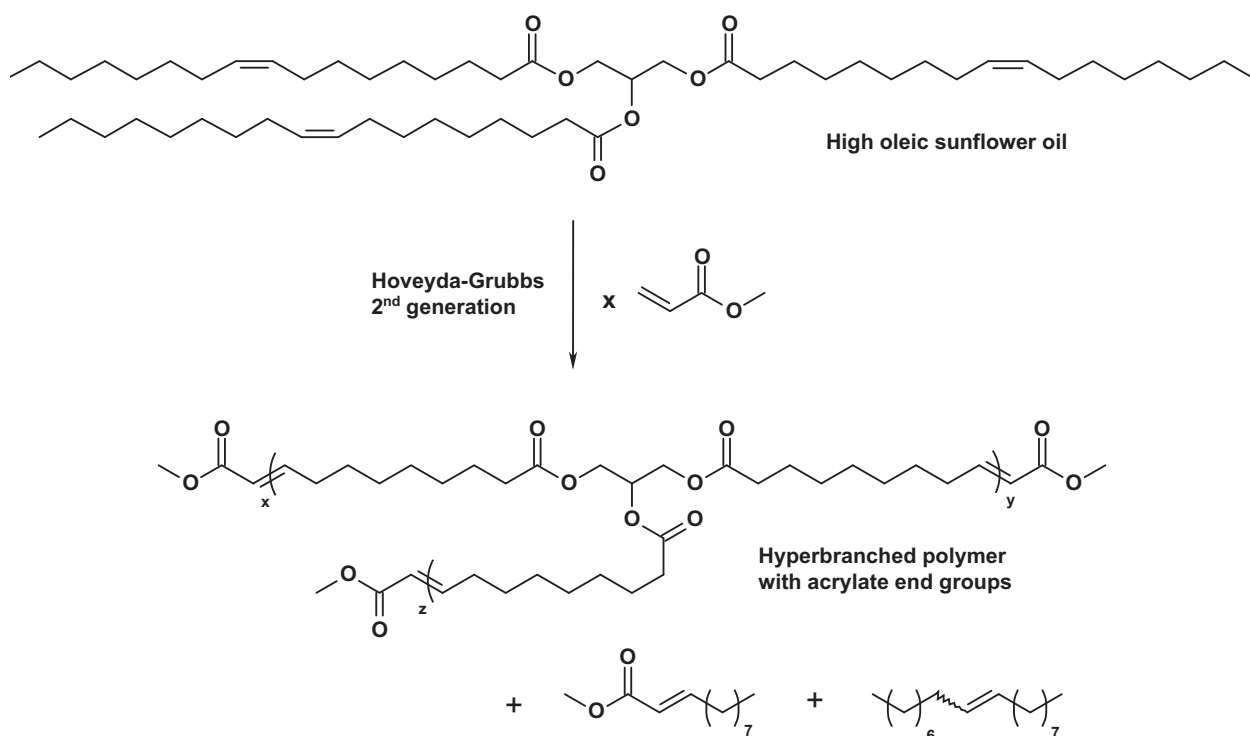


Fig. 11. One-step synthesis of end-group functionalized hyperbranched polymers from high oleic sunflower oil [61].

using different plant oil/chain stopper ratios were thoroughly analyzed by ESI-MS, and the results confirmed that highly branched polymers ranging from dimers to polymers were obtained.

The synthesis of cross-linked polymers from triglycerides is an active and wide field lead by several research groups. Larock's group has extensively studied the cross-linking of different plant oils *via* cationic polymerization in the presence of protic acids and Lewis acids. Among their important contributions is the finding that the introduction of small alkene comonomers such as styrene, divinylbenzene, norbornadiene, or dicyclopentadiene, is generally necessary to obtain thermosetting polymers ranging from soft rubbers to hard plastics [62], and that the most efficient catalyst for these curing systems is $\text{BF}_3 \cdot \text{Et}_2\text{O}$ for homopolymerizations, and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ modified with Norway fish oil ethyl ester for copolymerizations. Along the same lines, Sacristán et al. recently showed the possibility of reducing the curing process, from 12 to 1 h, when the cationic copolymerization of soybean oil with styrene and divinylbenzene was performed under microwave radiation [63]. Work in Larock's group has also been

devoted to the thermal copolymerization of tung [64] or linseed [65] oils with styrene and divinylbenzene, and to the radical copolymerization of conjugated plant oils with divinylbenzene, acrylonitrile, and dicyclopentadiene [66]. Moreover, they have recently focused on the ring opening metathesis polymerization (ROMP) of plant oil derivatives. Thus, a bicyclic derivative was obtained by reaction of castor oil with a commercial bicyclic anhydride. This compound was copolymerized *via* ROMP with cyclooctene (COE) to obtain transparent rubbery thermosets with oil contents between 55 and 85%, glass transition temperatures ranging from -14 to 1°C , and thermally stable below 200°C (Fig. 12) [67]. Similar materials were also obtained using Dilulin, a commercial mixture of norbornenyl functionalized linseed oil and cyclopentadiene oligomers. The ROMP of Dilulin with different polycyclic norbornene based comonomers afforded transparent thermosets from soft and flexible to hard and strong [68].

The synthesis of polyurethane networks from vegetable oils has been the subject of Petrovic's research group for a long time already [69]. Using the reactivity of the double bonds in triglycerides, they have explored different

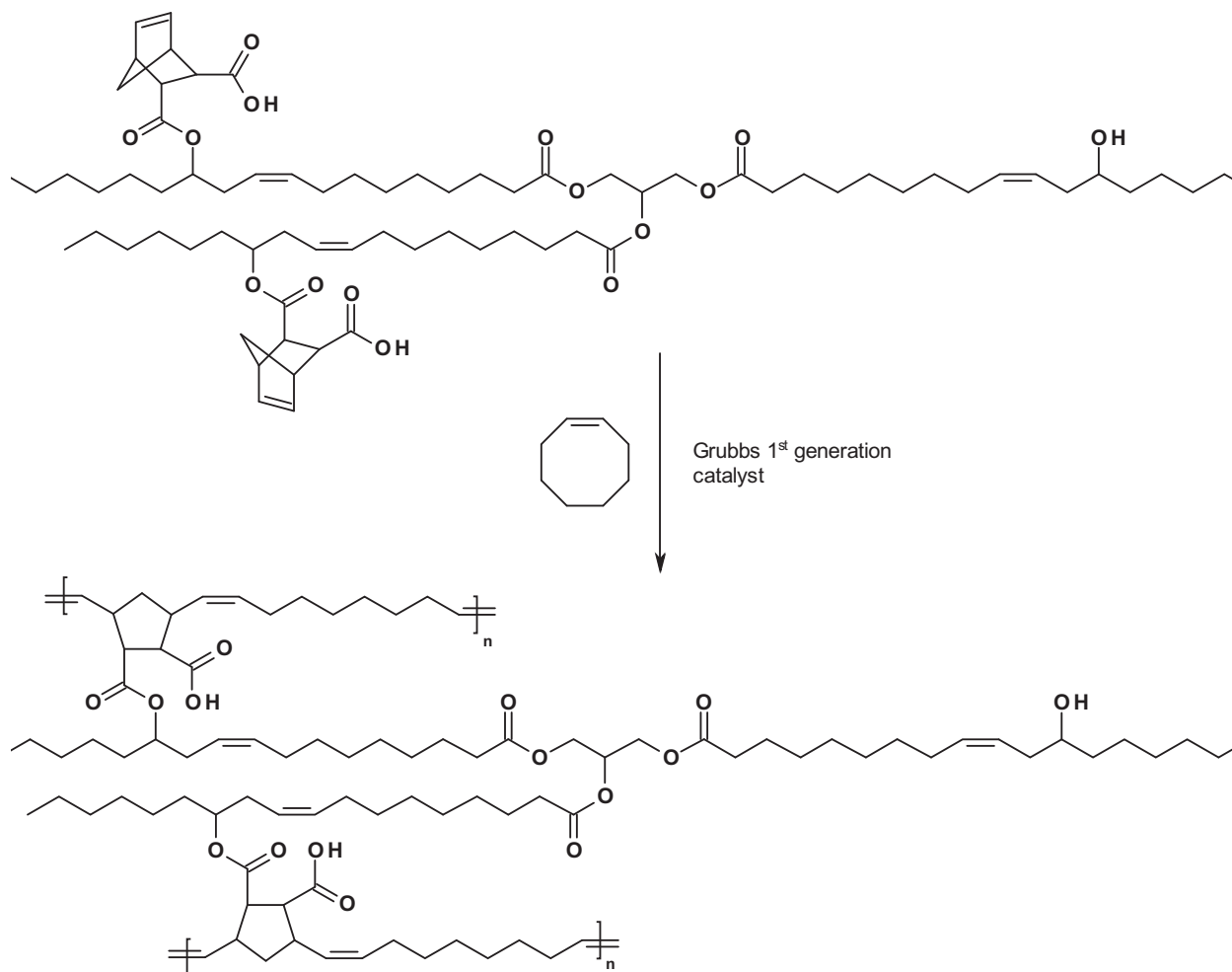


Fig. 12. Synthesis of castor oil derived thermosets *via* ROMP [67].

approaches to introduce hydroxyl groups, namely epoxidation–ring opening [70], ozonolysis [71], or hydroformylation [72], among others. These renewable polyols have been used for the preparation of cross-linked polyurethanes with varying properties depending on the plant oil used [70]. Also in this context, Lligadas et al. have recently reviewed different approaches to the synthesis of plant oil based polyols and the polyurethanes derived from them [73].

The groups of Kusefoglu and Wool have also investigated many different approaches to plant oil based thermosets both independently and in collaboration. Some examples include the radical polymerization of acrylated [74,75] or maleinized [74,76] plant oil derivatives, the direct cross-linking of soybean oil with polybutadiene [77] or *p*-dinitrosobenzene [78], and of linseed oil with phenolic resins [79], the synthesis of polyurethane foams [80], or the development of biocompatible adhesives [81]. Among other examples, Gandini and coworkers developed various acrylated plant oil derivatives and reported the study of their UV-curing [82]. Moreover, in recent studies, Sacristán et al. have shown the possibility of increasing the added-value of soybean oil based cross-linked polymers by inferring them fire retardant. This could be done by introducing silicon and boron containing comonomers in the cationic polymerization of soybean oil with styrene and divinylbenzene [83].

Thiol–ene addition reactions have also been applied to triglyceride derivatives for the synthesis of cross-linked

polymers. The reactivity of canola and corn oils towards butanethiol under UV irradiation was investigated by Bantchev et al. [84]. In order to optimize the reaction conditions, thiol–ene additions were performed varying different reaction parameters and the products were transesterified, thus allowing GC/GC–MS analysis of the resulting fatty acid methyl esters. The results revealed that, working under optimized reaction conditions, it was possible to obtain up to 97% of double bond conversion with an isolated yield of 61%. Very recently, Claudino et al. studied the effect of the *cis/trans* configuration of fatty acids on their reactivity in thiol–ene additions [85]. The reaction of an internal *cis*-alkene (methyl oleate) with a trithiol was found to consist of an insertion–isomerization–elimination sequence, which led to a very fast formation of the *trans*-isomer. This *cis/trans* isomerization dominated in the first steps of the reaction, and was followed by thiol addition. When a *trans*-alkene (methyl elaidate) was used as starting reagent, thiol addition took place at a higher rate. However, since the *cis/trans* isomerization was more rapid than the thiol addition, they found that the rate-determining step, in both cases, was the abstraction of hydrogen from the thiol groups by the intermediate carbon-centered radical. Although no cross-linked structures were reported, these studies provided valuable information concerning the reactivity of fatty acids and triglycerides. Regarding the development of cross-linked polymers, Black and Rowling prepared UV-cured films by reaction of allyl, acrylate, and vinyl ether derivatives of castor oil with multifunctional

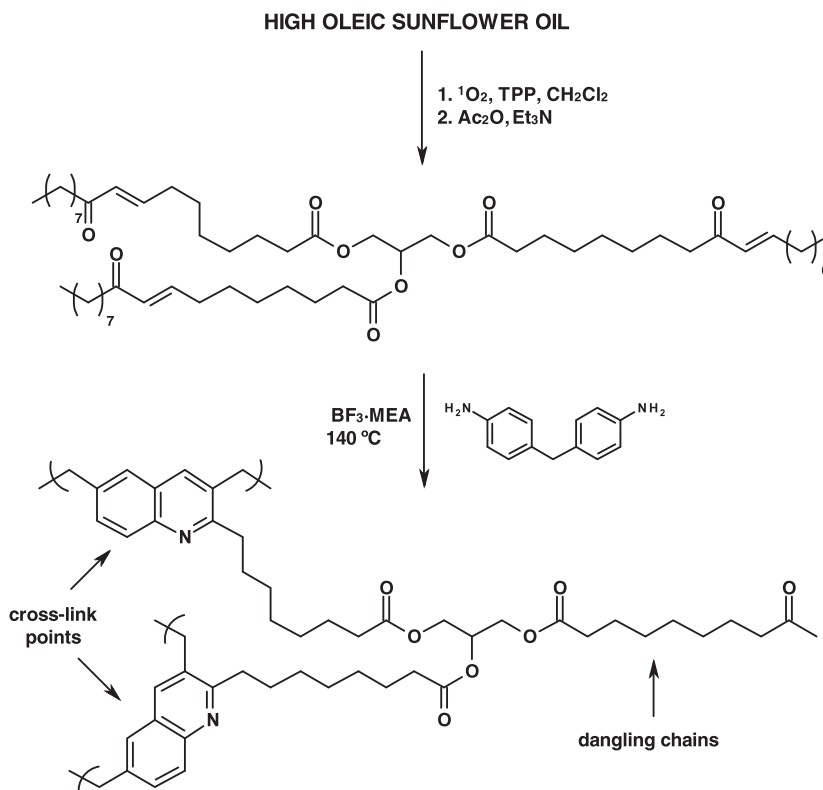


Fig. 13. Synthesis of thermosetting polymers with quinoline rings as cross-link sites from high oleic sunflower oil [91].

thiols [86]. Webster and coworkers recently prepared soybean oil based thiols and enes that were consequently used in the formulation of UV-curable films [87]. These multifunctional thiols and enes were synthesized by ring opening of epoxidized soybean oil with polythiols or allyl alcohol, respectively. These products with high functionality provided good coating film properties by UV-curing in the presence of petrochemical based enes or thiols.

These examples show how the reactivity of the internal double bonds of fatty acids has been exploited in very different ways to introduce polymerizable groups to triglycerides. However, little attention has been paid to the photochemical reactivity of triglyceride double bonds as a way to introduce polymerizable functionalities. Since the main reason of using plant oils as feedstock for polymer production is the renewability, the chemical transformations performed on them should also fulfil, as good as possible, the requirements of green chemistry. The photon is the green reagent par excellence, leaving no residue and inducing chemical transformations under mild conditions. Moreover, reactions *via* electronic excited states allow chemical transformations to take place through shorter paths than thermal alternatives and with excellent atom economy [88]. The singlet oxygen photoperoxidation of high oleic sunflower oil produces a triglyceride containing hydroperoxide groups, which can be either dehydrated to α,β -unsaturated ketones [89] (KSO) or reduced to allylic alcohols [90] (HSO). In this way, two different polyfunctional monomers can be easily prepared directly from an inexpensive (less than 1€/L) plant oil, after simple crystallization or washing purification steps.

KSO has been used in the synthesis of cross-linked polymers via aza-Michael reaction with 4,4'-diaminodiphenylmethane (DDM), an aromatic diamine commonly used as cross-linking agent for epoxy resins [89]. In fact, KSO showed clearly higher reactivity than its epoxidized counterpart towards cross-linking when reacted with DDM, even when a Lewis catalyst was added only to the epoxy system. Later on, the effect of $\text{BF}_3 \cdot \text{MEA}$ and the temperature on the products formed in the curing of KSO with DDM was studied. For this purpose, fatty acid model compounds and a monofunctional aromatic amine were used. It could be found that after the initial aza-Michael addition, a series of consecutive reactions promoted by $\text{BF}_3 \cdot \text{MEA}$ at temperatures over 100 °C take place [91]. First, the retro-Mannich type fragmentation of the addition product occurs, followed by self-aldol condensation, cyclization and aromatization reactions, which in the end lead to formation of substituted quinolines. This finding was exploited enabling the synthesis of plant oil-quinoline based networks with improved mechanical properties (Fig. 13).

The transformation of HSO into cross-linked networks involved the acrylation of the hydroxyl groups and radical polymerization in the presence of dicumyl peroxide [90]. The relation between cross-link density and mechanical properties was investigated by introducing different amounts of pentaerythritol tetraacrylate (PETA) as cross-linking agent. Moreover, the exhaustive hydrogenation of HSO gave saturated triglyceride HSO[H], which after acrylation and cross-linking with PETA led to an improvement

in the thermal stability of the thermosets. Once having established the possibility of obtaining cross-linked polymers from HSO, the following study aimed to improve their flame retardancy. Thus, the allylic hydroxyl groups of HSO were reacted with different amounts of chlorodiphenylphosphine *via* formation of allyl phosphinite and subsequent [2,3]-sigmatropic rearrangement [92]. In this way, the content of phosphorus could be controlled in such a way that free hydroxyl groups were left for acrylation. The subsequent radical polymerization with varying amounts of PETA provided a family of thermosets with improved fire resistance (increase of LOI from 19 to 22).

4. Conclusions

Plant oils and the fatty acids derived from them have been used for a long time by polymer chemists. Regarding the recent past, research developed by different groups reveals a growing interest in the reactivity of their double bonds towards olefin metathesis, which enables the straightforward synthesis of a wide variety of monomers. Moreover, the great potential of fatty acids as building blocks for olefin metathesis polymerization (ADMET) is now a reality. On the other hand, the production of monomers and polymers by thiol-ene coupling reactions with fatty acid derivatives is a newly growing area and we strongly believe that future will continue in this direction due to the vast, yet unexplored, possibilities of the thiol-ene/fatty acids combination. Furthermore, the versatility of plant oils as precursors of thermosetting materials has been demonstrated with the development of synthetic strategies leading to new polymeric materials. Also this development is far from an end and ever new possibilities for the chemical utilization of this renewable feedstock will certainly develop in all discussed fields.

References

- [1] (a) Meier MAR, Metzger JO, Schubert US. Plant oil renewable resources as green alternatives in polymer science. *Chem Soc Rev* 2007;36:1788–802;
(b) Metzger JO. Fats and oils as renewable feedstock for chemistry. *Eur J Lipid Sci Technol* 2009;111(9):865–76.
- [2] (a) Nayak PL. Natural oil-based polymers: opportunities and challenges. *Polym Rev* 2000;40(1):1–21;
(b) Güner FS, Yağcı Y, Erciyes AT. Polymers from triglyceride oils. *Prog Polym Sci* 2006;31(7):633–70;
(c) Sharma V, Kundu PP. Addition polymers from natural oils – a review. *Prog Polym Sci* 2006;31(11):983–1008;
(d) Sharma V, Kundu PP. Condensation polymers from natural oils. *Prog Polym Sci* 2008;33(12):1199–215.
- [3] Jérôme F, Pouilloux Y, Barrault J. Rational design of solid catalysts for the selective use of glycerol as a natural organic building block. *ChemSusChem* 2008;1(7):586–613.
- [4] (a) Biermann U, Friedt W, Lang S, Lühs W, Machmüller G, Metzger JO, et al. New syntheses with oils and fats as renewable raw materials for the chemical industry. *Angew Chem Int Ed* 2000;39(13):2206–24;
(b) Behr A, Gomes JP. The refinement of renewable resources: new important derivatives of fatty acids and glycerol. *Eur J Lipid Sci Technol* 2010;112(1):31–50;
(c) Köckritz A, Martin A. Oxidation of unsaturated fatty acid derivatives and vegetable oils. *Eur J Lipid Sci Technol* 2008;110(9):812–24.
- [5] Warwel S, Brüse F, Demes C, Kunz M, Rüschen gen. Klaas M. Polymers and surfactants on the basis of renewable resources. *Chemosphere* 2001;43(1):39–48.

- [6] Hurier C, Fischmeister C, Bruneau C, Olivier-Bourbigou H, Dixneuf P. Ethenolysis of methyl oleate in room-temperature ionic liquids. *ChemSusChem* 2008;1(1–2):118–22.
- [7] Schrodi Y, Ung T, Vargas A, Mkrtumyan G, Lee CW, Champagne TM, et al. Ruthenium olefin metathesis catalysts for the ethenolysis of renewable feedstocks. *Clean* 2008;36(8):669–73.
- [8] (a) Malacea R, Fischmeister C, Bruneau C, Dubois J-L, Couturier J-L, Dixneuf PH. Renewable materials as precursors of linear nitrile-acid derivatives via cross-metathesis of fatty esters and acids with acrylonitrile and fumaronitrile. *Green Chem* 2009;11:152–5; (b) Bruneau C, Fischmeister C, Miao X, Malacea R, Dixneuf PH. Cross-metathesis with acrylonitrile and applications to fatty acid derivatives. *Eur J Lipid Sci Technol* 2010;112(1):3–9.
- [9] Miao X, Fischmeister C, Bruneau C, Dixneuf P. A direct route to bifunctional aldehyde derivatives via self- and cross-metathesis of unsaturated aldehydes. *ChemSusChem* 2009;2(6):542–5.
- [10] Miao X, Blokhin A, Pasynskii A, Nefedov S, Osipov SN, Roisnel T, et al. Alkylidene–ruthenium–tin catalysts for the formation of fatty nitriles and esters via cross-metathesis of plant oil derivatives. *Organometallics* 2010. doi:10.1021/om100372b.
- [11] Rybak A, Meier MAR. Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry. *Green Chem* 2007;9:1356–61.
- [12] Djigoué GB, Meier MAR. Improving the selectivity for the synthesis of two renewable platform chemicals via olefin metathesis. *Appl Catal A* 2009;368(1–2):158–62.
- [13] Hong SH, Sanders DP, Lee CW, Grubbs RH. Prevention of undesirable isomerization during olefin metathesis. *J Am Chem Soc* 2005;127(49):17160–1.
- [14] Rybak A, Meier MAR. Cross-metathesis of oleyl alcohol with methyl acrylate: optimization of reaction conditions and comparison of their environmental impact. *Green Chem* 2008;10:1099–104.
- [15] Eissen M, Metzger JO. Environmental performance metrics for daily use in synthetic chemistry. *Chem Eur J* 2002;8(16):3580–5.
- [16] Ho TTT, Meier MAR. A design-of-experiments approach for the optimization and understanding of the cross-metathesis reaction of methyl acrylate with methyl ricinoleate. *ChemSusChem* 2009;2(8):749–54.
- [17] Jiménez-Rodríguez C, Eastham GR, Cole-Hamilton DJ. Dicarboxylic acid esters from the carbonylation of unsaturated esters under mild conditions. *Inorg Chem Commun* 2005;8(10):878–81.
- [18] Quinzler D, Mecking S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew Chem Int Ed* 2010;49(25):4306–8.
- [19] (a) Zhu Y, Patel J, Mujcinovic S, Jackson WR, Robinson AJ. Preparation of terminal oxygenates from renewable natural oils by a one-pot metathesis–isomerisation–methoxycarbonylation–transesterification reaction. *Green Chem* 2006;8:746–9; (b) Jimenez Rodriguez C, Foster DF, Eastham GR, Cole-Hamilton DJ. Highly selective formation of linear esters from terminal and internal alkenes catalysed by palladium complexes of bis-(di-tert-butylphosphinomethyl)benzene. *Chem Commun* 2004:1720–1.
- [20] Jacobs T, Rybak A, Meier MAR. Cross-metathesis reactions of allyl chloride with fatty acid methyl esters: efficient synthesis of α,ω -difunctional chemical intermediates from renewable raw materials. *Appl Catal A* 2009;353(1):32–5.
- [21] Mutlu H, Montero de Espinosa L, Meier MAR. Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures. *Chem Soc Rev* 2010. doi:10.1039/b924852b.
- [22] Mutlu H, Meier MAR. Castor oil as a renewable resource for the chemical industry. *Eur J Lipid Sci Technol* 2010;112(1):10–30.
- [23] Rybak A, Meier MAR. ADMET with a monomer from renewable resources: molecular weight control and one step block copolymer preparation. *ChemSusChem* 2008;1(6):542–7.
- [24] CTIF 9th Annual Report, June 2003. www.ctif.org.
- [25] Lu SY, Hamerton I. Recent developments in the chemistry of alkojen-free flame retardants. *Prog Polym Sci* 2002;27(8):1661–712.
- [26] Montero de Espinosa L, Ronda JC, Galià M, Cádiz V, Meier MAR. Fatty acid derived phosphorus-containing polyesters via acyclic diene metathesis (ADMET) polymerization. *J Polym Sci Part A: Polym Chem* 2009;47(21):5760–71.
- [27] Montero de Espinosa L, Meier MAR, Ronda JC, Galià M, Cádiz V. Phosphorus-containing renewable polyester–polyols via admnet polymerization. Synthesis, functionalization and radical cross-linking. *J Polym Sci Part A: Polym Chem* 2010;48(7):1649–60.
- [28] Bell BM, Briggs JR, Campbell RM, Chambers SM, Gaarenstroom PD, Hippler JG, et al. Glycerin as a renewable feedstock for epichlorohydrin production. The GTE process. *Clean* 2008;36(8):657–61.
- [29] Fokou PA, Meier MAR. Use of a renewable and degradable monomer to study the temperature-dependent olefin isomerization during ADMET polymerizations. *J Am Chem Soc* 2009;131(5):1664–5.
- [30] Fokou PA, Meier MAR. Studying and suppressing olefin isomerization side reactions during ADMET polymerizations. *Macromol Rapid Commun* 2010;31(4):368–73.
- [31] Mutlu H, Montero de Espinosa L, Türlüç O, Meier MAR. About the activity and selectivity of less well known metathesis catalysts during ADMET polymerizations. *Beilstein J Org Chem* 2010;6:1149–58. doi:10.3762/bjoc.6.131.
- [32] Kreye O, Tóth T, Meier MAR. Poly- α,β -unsaturated aldehydes derived from castor oil via ADMET polymerization. *Eur J Lipid Sci Technol*, accepted for publication.
- [33] Mutlu H, Meier MAR. Unsaturated PA X₂₀ from renewable resources via metathesis and catalytic amidation. *Macromol Chem Phys* 2009;210(12):1019–25.
- [34] Leitgeb A, Wappel J, Slugovc C. The ROMP toolbox upgraded. *Polymer* 2010;51(14):2927–46.
- [35] Mutlu H, Meier MAR. Living ring opening metathesis polymerization of fatty acid derived monomers. *J Polym Sci Part A: Polym Chem* 2010;48(24):5899–906. doi:10.1002/pola.24401.
- [36] Çaylı C, Meier MAR. Polymers from renewable resources: bulk ATRP of fatty alcohol derived methacrylates. *Eur J Lipid Sci Technol* 2008;110(9):853–9.
- [37] (a) Becer CR, Hoogenboom R, Schubert U. Click chemistry beyond metal-catalyzed cycloaddition. *Angew Chem Int Ed* 2009;48(27):4900–8; (b) Hoyle CE, Bowman CN. Thiol–ene click chemistry. *Angew Chem Int Ed* 2010;49(9):1540–73.
- [38] Lowe AB. Thiol–ene “click” reactions and recent applications in polymer and materials synthesis. *Polym Chem* 2010;1:17–36.
- [39] Koenig NH, Swern D. Organic sulfur derivatives. I. Addition of mercaptoacetic acid to long-chain monounsaturated compounds. *J Am Chem Soc* 1957;79(2):362–5.
- [40] Metzger JO, Riedner U. Radikalische Additionen an ungesättigte Fettstoffe. *Fat Sci Technol* 1989;91(1):18–23.
- [41] Samuelsson J, Jonsson M, Brinck T, Johansson M. Thiol–ene coupling reaction of fatty acid derived monomers. *J Polym Sci Part A: Polym Chem* 2004;42(24):6346–52.
- [42] Lluch C, Ronda JC, Galià M, Lligadas G, Cádiz V. Rapid approach to biobased telechelics through two one-pot thiol–ene click reactions. *Biomacromolecules* 2010;11(6):1646–53.
- [43] Türlüç O, Meier MAR. Fatty acid derived monomers and related polymers via thiol–ene (click) additions. *Macromol Rapid Commun* 2010;31(20):1822–6.
- [44] Hoogenboom R, Schubert US. Microwave-assisted cationic ring-opening polymerization of a soy-based 2 oxazoline monomer. *Green Chem* 2006;8:895–9.
- [45] Hoogenboom R, Thijs HML, Fijtjen MWM, Schubert US. Synthesis, characterization, and cross-linking of a library of statistical copolymers based on 2-“soy alkyl”-2-oxazoline and 2-ethyl-2-oxazoline. *J Polym Sci Part A: Polym Chem* 2007;45(23):5371–9.
- [46] Huang H, Hoogenboom R, Leenen MAM, Guillet P, Jonas AM, Schubert US, et al. Solvent-induced morphological transition in core-cross-linked block copolymer micelles. *J Am Chem Soc* 2006;128(11):3784–8.
- [47] Del Rio E, Galià M, Cádiz V, Lligadas G, Ronda JC. Polymerization of epoxidized vegetable oil derivatives: ionic-coordinative polymerization of methylepoxyoleate. *J Polym Sci Part A: Polym Chem* 2010;48(22):4995–5008.
- [48] Del Rio E, Lligadas G, Ronda JC, Galià M, Cádiz V. Biobased polyurethanes from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate. *J Polym Sci Part A: Polym Chem* 2010;48(22):5009–17.
- [49] Lligadas G, Ronda JC, Galià M, Cádiz V. Polyurethane networks from fatty-acid-based aromatic triols: synthesis and characterization. *Biomacromolecules* 2007;8(6):1858–64.
- [50] Yue J, Narine SS. Synthesis of aromatic triols and triacids from oleic and erucic acid: separation and characterization of the asymmetric and symmetric isomers. *Chem Phys Lipids* 2008;152(1):1–8.
- [51] Hojabri L, Kong X, Narine SS. Fatty acid-derived diisocyanate and biobased polyurethane produced from vegetable oil: synthesis, polymerization, and characterization. *Biomacromolecules* 2009;10(4):884–91.
- [52] Hojabri L, Kong X, Narine SS. Novel long chain unsaturated diisocyanate from fatty acid: synthesis, characterization, and application in bio-based polyurethane. *J Polym Sci Part A: Polym Chem* 2010;48(15):3302–10.

- [53] Hojabri L, Kong X, Narine SS. Functional thermoplastics from linear diols and diisocyanates produced entirely from renewable lipid sources. *Biomacromolecules* 2010;11(4):911–8.
- [54] Liu G, Kong X, Wan H, Narine S. Production of 9-hydroxynonanoic acid from methyl oleate and conversion into lactone monomers for the synthesis of biodegradable polylactones. *Biomacromolecules* 2008;9(3):949–53.
- [55] Abraham S, Narine SS. Polynonanolactone synthesized from vegetable oil: evaluation of physical properties, biodegradation, and drug release behavior. *J Polym Sci Part A: Polym Chem* 2009;47(23):6373–87.
- [56] Sokolsky-Papkov M, Shikanov A, Kumar N, Vaisman B, Domb AJ. Fatty acid based biodegradable polymers – synthesis and applications. *Bull Israel Chem Soc* 2008;23:12–7.
- [57] Refvik MD, Larock RC. The chemistry of metathesized soybean oil. *J Am Oil Chem Soc* 1999;76(1):99–102.
- [58] Refvik MD, Larock RC, Tian Q. Ruthenium-catalyzed metathesis of vegetable oils. *J Am Chem Oil Soc* 1999;76(1):93–8.
- [59] Tian Q, Larock RC. Model studies and the ADMET polymerization of soybean oil. *J Am Chem Oil Soc* 2002;79(5):479–88.
- [60] Fokou PA, Meier MAR. Acyclic triene metathesis (ATMET) polymerization with chain-stoppers: molecular weight control in the synthesis of branched polymers. *Macromol Rapid Commun* 2008;29(19):1620–5.
- [61] Biermann U, Metzger JO, Meier MAR. Acyclic triene metathesis oligo- and polymerization of high oleic sun flower oil. *Macromol Chem Phys* 2010;211(8):854–62.
- [62] Lu Y, Larock RC. Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications. *ChemSusChem* 2009;2(2):136–47.
- [63] Sacristán M, Ronda JC, Galià M, Cádiz V. Rapid soybean oil copolymers synthesis by microwave-assisted cationic polymerization. *Macromol Chem Phys* 2010;211(7):801–8.
- [64] Li F, Larock RC. Synthesis, structure and properties of new tung oil-styrene-divinylbenzene copolymers prepared by thermal polymerization. *Biomacromolecules* 2003;4(4):1018–25.
- [65] Kundu PP, Larock RC. Novel conjugated linseed oil-styrene-divinylbenzene copolymers prepared by thermal polymerization. Effect of monomer concentration on the structure and properties. *Biomacromolecules* 2005;6(2):797–806.
- [66] (a) Henna PH, Andjelkovic DD, Kundu PP, Larock RC. Biobased thermosets from the free-radical copolymerization of conjugated linseed oil. *J Appl Polym Sci* 2007;104(2):979–85; (b) Valverde M, Andjelkovic DD, Kundu PP, Larock RC. Conjugated low-saturation soybean oil thermosets: free-radical copolymerization with dicyclopentadiene and divinylbenzene. *J Appl Polym Sci* 2008;107(1):423–30.
- [67] Henna PH, Larock RC. Rubbery thermosets by ring-opening metathesis polymerization of a functionalized castor oil and cyclooctene. *Macromol Mater Eng* 2007;292(12):1201–9.
- [68] (a) Henna PH, Kessler MR, Larock RC. Fabrication and properties of vegetable-oil-based glass fiber composites by ring-opening metathesis polymerization. *Macromol Mater Eng* 2008;293(12):979–90; (b) Mauldin TC, Haman K, Sheng X, Henna P, Larock RC, Kessler MR. Ring-opening metathesis polymerization of a modified linseed oil with varying levels of crosslinking. *J Polym Sci Part A: Polym Chem* 2008;46(20):6851–60.
- [69] Petrovic ZS. Polyurethanes from vegetable oils. *Polym Rev* 2008;48(1):109–55.
- [70] Zlatanovic A, Lava C, Zhang W, Petrovic ZS. Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J Polym Sci Part B: Polym Phys* 2004;42(5):809–19.
- [71] Petrovic ZS, Zhang W, Javni I. Physical properties of canola oil based polyurethane networks. *Biomacromolecules* 2005;6(2):713–9.
- [72] Petrovic ZS, Guo A, Javni I, Cvetkovic I, Pyo D. Hong Polyurethane networks from polyols obtained by hydroformylation of soybean oil. *Polym Int* 2008;57(2):275–81.
- [73] Lligadas G, Ronda JC, Galià M, Cádiz V. Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art. *Biomacromolecules* 2010. doi:10.1021/bm100839x.
- [74] Khot SN, Lascala JJ, Can E, Morye SS, Williams GI, Palmese GR, et al. Development and application of triglyceride-based polymers and composites. *J Appl Polym Sci* 2001;82(3):703–23.
- [75] Eren T, Küsefoglu SH. Synthesis and polymerization of the bromoacrylated plant oil triglycerides to rigid, flame-retardant polymers. *J Appl Polym Sci* 2004;91(4):2700–10.
- [76] Can E, Wool RP, Küsefoglu SH. Soybean- and castor-oil-based thermosetting polymers: mechanical properties. *J Appl Polym Sci* 2006;102(2):1497–504.
- [77] Yilmaz M, Küsefoglu SH. Gelation of soybean oil with polybutadiene. *J Appl Polym Sci* 2005;96(1):2240–6.
- [78] Mutlu H, Küsefoglu SH. Synthesis and characterization of polymers from soybean oil and p-dinitrosobenzene. *J Appl Polym Sci* 2009;113(3):1925–34.
- [79] Çaylı G, Küsefoglu SH. Polymerization of linseed oil with phenolic resins. *J Appl Polym Sci* 2010;118(2):849–56.
- [80] Campanella A, Bonnaillie LM, Wool RP. Polyurethane foams from soybean-based polyols. *J Appl Polym Sci* 2009;112(4):2567–78.
- [81] Klapperich CM, Noack CL, Kaufman JD, Zhu L, Bonnaillie L, Wool RP. A novel biocompatible adhesive incorporating plant-derived monomers. *J Biomed Mater Res A* 2009;91A(2):378–84.
- [82] (a) Pelletier H, Belgacem N, Gandini A. Acrylated vegetable oils as photocrosslinkable materials. *J Appl Polym Sci* 2006;99(6):3218–21; (b) Pelletier H, Gandini A. Preparation of acrylated and urethanated triacylglycerols. *Eur J Lipid Sci Technol* 2006;108(5):411–20.
- [83] (a) Sacristán M, Ronda JC, Galià M, Cádiz V. Silicon containing soybean-oil-based copolymers. Synthesis and properties. *Biomacromolecules* 2009;10(9):2678–85; (b) Sacristán M, Hull TR, Stec AA, Ronda JC, Galià M, Cádiz V. Cone calorimetry studies of fire retardant soybean-oil-based copolymers containing silicon or boron: comparison of additive and reactive approaches. *Polym Degrad Stab* 2010;95(7):1269–74.
- [84] Bantchev GB, Kenar JA, Biresaw G, Han MG. Free radical addition of butanethiol to vegetable oil double bonds. *J Agric Food Chem* 2009;57(4):1282–90.
- [85] Claudino M, Johansson M, Jonsson M. Thiol-ene coupling of 1,2-disubstituted alkene monomers – the kinetic effect of cis/trans-isomer structures. *Eur Polym J* 2010;46(12):2321–32.
- [86] Black M, Rawlins JW. Thiol-ene UV-curable coatings using vegetable oil macromonomers. *Eur Polym J* 2009;45(5):1433–41.
- [87] Chen Z, Chisholm BJ, Patani R, Wu JF, Fernando S, Jogodzinski K, et al. Soy-based UV-curable thiol-ene coatings. *J Coat Technol Res* 2010;7(5):603–13.
- [88] Albini A, Fagnoni M. Photochemistry as a green synthetic method. In: Mordini A, Faigl F, editors. *New methodologies and techniques for a sustainable organic chemistry*. Dordrecht: Springer; 2008. p. 279–93.
- [89] Montero de Espinosa L, Ronda JC, Galià M, Cádiz V. A new enone-containing triglyceride derivative as precursor of thermosets from renewable resources. *J Polym Sci Part A: Polym Chem* 2008;46(20):6843–50.
- [90] Montero de Espinosa L, Ronda JC, Galià M, Cádiz V. A new route to acrylated oils. Crosslinking and properties of acrylated triglycerides from high oleic sunflower oil. *J Polym Sci Part A: Polym Chem* 2009;47(4):1159–67.
- [91] Montero de Espinosa L, Ronda JC, Galià M, Cádiz V. Quinoline-containing networks from enone and aldehyde triglyceride derivatives. *J Polym Sci Part A: Polym Chem* 2010;48(4):869–78.
- [92] Montero de Espinosa L, Ronda JC, Galià M, Cádiz V. A straightforward strategy for the efficient synthesis of acrylate and phosphine oxide-containing vegetable oils and their crosslinked materials. *J Polym Sci Part A: Polym Chem* 2009;47(16):4051–63.



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